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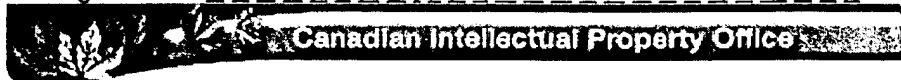
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## Canadian Patents Database

(12) Patent Application:

(11) CA 2127919

(54) PROCESS FOR PRODUCING ULTRAFINE SIZED LATEXES

(54) PROCEDE DE PRODUCTION DE LATEX ULTRAFINS

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### ABSTRACT:

#### ABSTRACT OF THE DISCLOSURE

A process for producing an aqueous-based dispersion containing between about 15 and about 50 percent by weight solids comprising the steps of:

- (a) incrementally adding one or more ethylenically unsaturated monomers capable of polymerizing in an aqueous environment to a reaction vessel containing water and up to 6.3 parts per hundred parts monomers of one or more surfactants;
- (b) incrementally adding one or more polymerization initiators to said reaction vessel; and
- (c) allowing said one or more ethylenically unsaturated monomers to polymerize such that the average particle size of said polymerized monomers is less than 100 nanometers; and the dispersion produced therein is disclosed. The produced dispersions have a wide range of practical uses.

CLAIMS: [Show all claims](#)

\*\*\* Note: Data on abstracts and claims is shown in the official language in which it was submitted.

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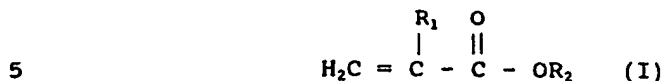


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## WHAT IS CLAIMED IS:

1. A process for producing an aqueous-based dispersion containing  
5 between about 15 and about 50 percent by weight solids comprising  
the steps of:
- (a) incrementally adding one or more ethylenically unsaturated  
10 monomers capable of polymerizing in an aqueous environment to  
a reaction vessel containing water and up to 6.3 parts per 100  
parts of said monomers of one or more surfactants;
- (b) incrementally adding one or more polymerization initiators  
15 to said reaction vessel; and
- (c) allowing said one or more ethylenically unsaturated  
monomers to polymerize such that the average particle size of  
said polymerized monomers is less than 100 nanometers.
- 20 2. The process according to claim 1 wherein steps (a) and (b)  
occur simultaneously.
3. The process according to claim 1 wherein said one or more  
25 ethylenically unsaturated monomers are selected from the group  
consisting of (meth)acrylic based acids and esters, acrylonitrile,  
styrene, divinylbenzene, vinyl acetate, ethylenically unsaturated  
carboxylic acids, butadiene, acrylamide, methacrylamide, vinylidene  
chloride, vinyl chloride and mixtures thereof.

4. The process according to claim 3 wherein said one or more ethylenically unsaturated monomers is of formula (I)



where  $\text{R}_1$  is hydrogen or an alkyl group having from 1 to 4 carbon atoms and  $\text{R}_2$  is an aliphatic group having from 1 to 20 carbon atoms.

10

5. The process according to claim 4 wherein said one or more ethylenically unsaturated monomers is selected from the group consisting of methyl methacrylate, ethyl acrylate, butyl acrylate, methacrylic acid, acrylic acid and mixtures thereof.

15

6. The process according to claim 3 wherein said one or more surfactants is selected from the group consisting of anionic, nonionic, cationic, amphoteric, and copolymerizable surfactants.

20

7. The process according to claim 6 wherein said one or more surfactants comprises one or more anionic surfactants present in an amount of about 0.5 to about 3.0 percent by weight of the amount of total monomers added.

25

8. The process according to claim 7 wherein said anionic surfactant is selected from the group consisting of water soluble salts of alkyl benzene sulfonates having between 8 and 22 carbon atoms in the alkyl group, alkyl ether sulfates having between 8 and 22 carbon atoms in the alkyl group, and alkali metal, ammonium and alkanolammonium salts or organic sulfuric reaction products having in their molecular structure an alkyl, or alkaryl group containing from 8 to 22 carbon atoms and a sulfonic or sulfuric acid ester group and mixtures thereof.

30

9. The process according to claim 8 wherein said anionic surfactant is selected from the group consisting of linear sodium and potassium alkyl sulfates and alkyl benzene sulfonates, in which the alkyl group contains between about 9 to about 15 carbon atoms, and mixtures thereof.
10. The process according to claim 9 wherein said anionic surfactant is sodium lauryl sulfate.
11. The process according to claim 3 wherein said polymerization initiator comprises a water soluble or organic soluble initiator which is fed in an amount ranging from about 0.1 to 3 percent by weight of said one or more ethylenically unsaturated monomers.
12. The process according to claim 11 wherein said polymerization initiator is soluble in said one or more ethylenically unsaturated monomers and is selected from the group consisting of azo, peroxide, perester and redox initiators.
13. The process according to claim 12 wherein said polymerization initiator is selected from the group consisting of 2,2'-azobis-isobutyronitrile, 2,2'-azobis-(2-methylpropanenitrile), 2,2'-azobis-(2,4-dimethylpentanenitrile), 2,2'-azobis-(2-methylbutanenitrile), 1,1'-azobis-(cyclohexanecarbonitrile), 2,2'-azobis-(2,4-dimethylvaleronitrile), 2,2'-azobis-(2,4-dimethyl-4-methoxyvaleronitrile) and 2,2'-azobis-(2-amidinopropane) hydrochloride.
14. The process according to claim 12 wherein said polymerization initiator is fed from the same vessel as said one or more ethylenically unsaturated monomers.
15. The process according to claim 11 wherein said polymerization initiator is water soluble and is added to said reaction vessel such that the reaction vessel maintains the same ionicity

throughout the polymerization reaction.

16. The process according to claim 15 wherein said polymerization initiator comprises a persulfate.

5

17. The process according to claim 3 comprising the additional step of adding between 0.5 and 10 percent by weight of said monomers added of any of the following materials to said dispersion: plasticizers, defoamers, pigments, colorants, dyes, antibacterials, perfumes, pharmaceuticals, enzymes, biologically active agents, agricultural chemicals, ultraviolet active agents, stabilizers, rheology modifiers, cross-linking agents and mixtures thereof.

10

18. The process according to claim 3 wherein said reaction occurs at a temperature ranging from about 40°C to about 80°C.

15

19. An aqueous-based dispersion containing between about 15 and about 50 percent by weight solids produced by a process comprising the steps of:

20

(a) incrementally adding one or more ethylenically unsaturated monomers capable of polymerizing in an aqueous environment to a reaction vessel containing water and up to 6.3 parts per hundred parts of said monomers of one or more surfactants;

25

(b) incrementally adding one or more polymerization initiators to said reaction vessel; and

30

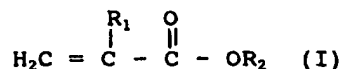
(c) allowing said one or more ethylenically unsaturated monomers to polymerize such that the average particle size of said polymerized monomers is less than 100 nanometers.

20. The dispersion according to claim 19 wherein said one or more ethylenically unsaturated monomers are selected from the group consisting of (meth)acrylic based acids and esters, acrylonitrile,

35

styrene, divinylbenzene, vinyl acetate, ethylenically unsaturated carboxylic acids, acrylamide, methacrylamide, butadiene, vinylidene chloride, vinyl chloride and mixtures thereof.

- 5 21. The dispersion according to claim 20 wherein said one or more ethylenically unsaturated monomers is of formula (I)



10

where  $\text{R}_1$  is hydrogen or an alkyl group having from 1 to 4 carbon atoms and  $\text{R}_2$  is an aliphatic group having from 1 to 20 carbon atoms.

- 15 22. The dispersion according to claim 21 wherein said one or more ethylenically unsaturated monomers is selected from the group consisting of methyl methacrylate, ethyl acrylate, butyl acrylate, methacrylic acid, acrylic acid and mixtures thereof.

- 20 23. The dispersion according to claim 20 wherein said dispersion contains between about 20 and about 40 percent by weight solids.

24. The dispersion according to claim 23 wherein said dispersion contains between about 25 and about 35 percent by weight solids.

25

25. The dispersion according to claim 20 having an average particle size of between about 1 and about 60 nanometers.

30

26. The dispersion according to claim 25 having an average particle size of between about 5 and about 40 nanometers.

27. The dispersion according to claim 26 having an average particle size of between about 10 and about 30 nanometers.

- 35 28. The dispersion according to claim 27 having an average particle

size of between about 10 and about 20 nanometers.

5 29. The dispersion according to claim 25 containing between 0.5 and 3 percent by weight of said total monomers added of said surfactant.

10 30. The dispersion according to claim 29 wherein said surfactant is selected from the group consisting of linear sodium and potassium alkyl ether sulfates and alkyl benzene sulfonates, in which the alkyl group contains between about 9 to about 15 carbon atoms, and mixtures thereof.

15 31. The dispersion according to claim 25 further comprising between about 0.5 and about 10 percent by weight of said monomers added of any of the following materials: plasticizers, defoamers, pigments, colorants, dyes, antibacterials, perfumes, pharmaceuticals, enzymes, biologically active agents, agricultural chemicals, ultraviolet active agents, stabilizers, rheology modifiers, cross-linking agents and mixtures thereof.

20 32. The use of the dispersion according to claim 25 as a wood preservative, polymer or metal coating, adhesive, waterproofing chemical, textile size, agricultural chemical, pharmaceutical, oil field chemical, ink, paper making chemical, rheology modifier, 25 cosmetic, personal care product, ultraviolet light scatterer, sunscreen, biomedical application or immunoassay application.

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RD93034

## PROCESS FOR PRODUCING ULTRAFINE SIZED LATEXES .

Background of the Invention

## 5 1. Field of the Invention

The present invention relates to extremely fine-sized aqueous polymeric dispersions, and particularly acrylic-based dispersions having a mean particle size of less than 60 nanometers. More specifically, the aqueous polymeric dispersions of the present invention are made by incremental addition of monomer and initiator solutions to an aqueous solution containing at least one emulsifier maintained in a minor amount.

## 15 2. Technology Description

Heretofore, numerous emulsion latexes have existed. However, the particle sizes of such latexes have generally been large, for example 120 nanometers or larger.

20 U.S. Patent No. 4,177,177 to Vanderhoff et al relates to various methods for making polymeric emulsions which can be utilized to produce latexes. The latexes generally have a particle size greater than 100 nanometers.

25 U.S. Patent No. 4,228,047 to Pippin et al relates to an aqueous coating composition comprising a copolymer of at least 95 percent by weight of vinyl acetate and at least 0.1 percent by weight of maleic anhydride which allegedly has been found to have improved starch binder compatibility.

30

Japanese Disclosure No. 52103588 to Asahi Dow relates to a carpet-backing composition containing 100 parts by weight (as solids content) of a copolymer latex: 200 to 350 parts by weight of inorganic filler and thickener consisting of 30-60 weight percent of a) butadiene: 20-70 weight percent of b) styrene 5-30 weight percent of c) methyl methacrylate: and 1 to 5 weight percent of d) ethylene series of unsaturated carboxylic acid and has an average particle diameter of 60 to 120 nm. By using the latex of small particle diameter for the carpet backing, blistering is prevented.

Belgian Patent No. 812139 to DeSoto, Inc. relates to opaque coatings obtained from a latex comprised of an aqueous suspension of small and large resin particles, the large particles having a  $T_g$  less than the small ones and having an average diameter which is greater than twice that of the small particles, the latter forming 20 to 65 weight percent of the total particles. The particles are such that neither the large nor the small ones can, on their own, coalesce when the latex is dried, to form a non-cellular film. The small particles actually give a powder under such conditions. The small particles are preferably polystyrene and the large ones a copolymer of vinyl acetate and an ester of a 4 to 18 carbon atom alkanol and an unsaturated carboxylic acid. The composition contains a minimum amount of solvent and rapidly gives an opaque coating of low porosity upon drying. It may be used for lipstick, crayons, etc.

British Patent No. 1,100,569 to the Dow Chemical Co. relates to acrylic polymer latexes containing large and small particles prepared by 1) heating water containing a soluble catalyst to up to 85°C in an inert atmosphere, 2) adding 1/3 of a mixture of monomers, 3) carrying on the polymerization for at least 15 minutes, 4) adding an aqueous solution of an anionic emulsifier and an aqueous solution of the polymerization catalyst, and 5) adding the remaining monomer continuously over a period of at least 45 minutes.

U.S. Patent No. 3,711,435 to DuPont and Co. relates to a stable, aqueous colloidal dispersion prepared by mixing 1) a copolymer of 20 to 80 weight percent ethylene and 80 to 20 weight percent of an aminoalkylacrylate; 2) an acid having a dissociation constant of 10 to 5; and 3) water in proportion to give a solids containing 5 to 30 weight percent and a degree of neutralization of the amino groups of the polymer of at least 40 percent. The mixing is effected at a temperature suitable for dispersing the polymer in particles of size less than 10 nanometers. The resulting dispersions have very small particle sizes so that they may be thinly spread over aluminum substrates to give void free coatings, and as flocculants for removal of suspended matter from water. N,N-dimethylaminoethylmethacrylate is a suitable comonomer.

Japanese Disclosure No. 52-123478 to Kurraray relates to compositions prepared by emulsion polymerization of unsaturated monomers in the presence of a protective colloid which is prepared by cleaving water-solubilized copolymers in the presence of free radicals and by heating. The compound contains units of maleinimide and/or N-substituted maleinimide and units of alpha-olefin as essential components of the main chain.

An article by Ugelstad, El-Aasser, and Vanderhoff, Journal of Polymer Science, Polymer Letters Edition, 11, 503: 1973 relates to the production of latex particles by mini-emulsion polymerization of a mixed-emulsifier system including a surfactant and a long-chain alcohol or alkane cosurfactant utilizing ultrasonification.

An article by Atik and Thomas, Journal of American Chemical Society, 101, 4279: 1981 relates to aqueous styrene polymer microemulsions made by bulk polymerization having a number average particle size of from about 20 to about 35 nanometers by utilizing a mixed emulsifier of cetyl-trimethylammonium bromide and hexanol followed by polymerization with an oil soluble azobisisobutyronitrile and irradiation. However, the solids

content was very low, less than 2 percent and the amount of emulsifiers utilized was approximately 1.5 times the amount of polymer by weight.

- 5 An article by Jayakrishnan and Shah, Journal of Polymer Science, Polymer Letters, 22, 31 984 relates to a bulk polymerization of polystyrene or methyl methacrylate microemulsion particles having a number average size of from about 10 to about 60 nanometers utilizing sodium dihexylsulfosuccinate and ethylene oxide-propylene
- 10 oxide block copolymers as mixed-emulsifiers and an oil soluble initiator such as benzoyl peroxide. However, the weight ratio of the emulsifier to the monomer was approximately one to one and the microemulsion could not be diluted with water.
- 15 Canadian Patent Application No. 2,013,318, assigned to B.P. Goodrich is directed to a process for producing very fine-sized aqueous polymeric microemulsions. The process utilizes incremental addition of a monomer feed solution into an aqueous solution including one or more emulsifying agents and one or more water
- 20 soluble or redox initiators. While this method may be used to produce such microemulsions, it is deficient in that the emulsion tends to discolor and that it is extremely difficult to obtain emulsions having a narrow particle size range profile.
- 25 An article by Okuba et al, "Preparation of Asymmetric Polymer Film by Emulsion Blend Technique", Colloid & Polymer Science, 268:1113-1117 (1990), teaches blending two different particle size emulsions together to determine the tackiness properties of such blends. One of the starting emulsions disclosed is a poly(ethyl acrylate-methyl
- 30 methacrylate) emulsion having a particle size of 0.02 microns. According to the article, this emulsion is prepared by combining the monomers in a glass flask with water, sodium sulfite, potassium persulfate and sodium dodecyl sulfate. The order or method of addition of the different reactants, initiators and emulsifiers is
- 35 not specified.

European Published Patent Application No. 0 429 207, assigned to Rohm & Haas is directed to a method of treating or coating a substrate with an aqueous composition. The coating composition is an aqueous dispersion of copolymer particles having mutually incompatible phases and having an average particle size of about 20 to about 70 nanometers. The dispersion is prepared by emulsion polymerization techniques. In preferred embodiments, the particles are of a core/shell morphology where the core has a  $T_g$  of at least 45°C and the shell has a  $T_g$  of lower than 35°C.

Despite the above teachings, there still exists a need in the art for a method to produce ultrafine sized emulsion latexes which do not discolor, have a narrow particle size distribution, are easily reproducible, and utilizes a minimal amount of surfactant.

#### Summary of the Invention

In accordance with the present invention, a process for producing ultrafine sized emulsion latexes which do not discolor, have a narrow particle size distribution, are easily reproducible, and utilizes a minimal amount of surfactant is provided. The process is particularly characterized by incrementally feeding monomers and initiators into an aqueous reaction medium such that the ionicity of the reaction medium remains constant.

One embodiment of the invention comprises a process for producing an aqueous-based dispersion containing between about 15 and about 50 percent by weight solids comprising the steps of:

- (a) incrementally adding one or more ethylenically unsaturated monomers capable of polymerizing in an aqueous environment to a reaction vessel containing water and up to 6.3 parts per 100 parts of said monomers of one or more surfactants;

(b) incrementally adding one or more polymerization initiators to said reaction vessel; and

5 (c) allowing said one or more ethylenically unsaturated monomers to polymerize such that the average particle size of said polymerized monomers is less than 100 nanometers.

10 In preferred embodiments, the process utilizes monomers derived from acrylic based acids and esters and yields ultrafine sized latexes having a mean particle size of less than 50 nanometers.

15 Another embodiment of the present invention comprises the dispersion manufactured by the novel process. The polymeric ultrafine-sized latex is coagulation stable and thus can be diluted with water. The polymer particles have several physical attributes such as good film formation, penetration into porous substrates, very high surface area to volume ratio, monomodality and the like.

20 The novel dispersions can be used in the manufacture of wood preservatives, polymer and metal coatings, adhesives, waterproofing chemicals, textile sizes, agricultural chemicals, pharmaceuticals, oil field chemicals, inks, paper manufacture, rheology modifiers, cosmetics, ultraviolet light scatterers, biomedical and immunoassay applications.

25 An object of the present invention is to produce an ultrafine sized latex emulsion which does not discolor, has a narrow particle size distribution, is easily produced, and utilizes a minimal amount of surfactant.

30 An additional object of the present invention is to provide a ultrafine sized latex emulsion which is coagulation stable, has good film formation, penetration into porous substrates, very high surface area to volume ratio and monomodality.

35

These, as other objects, will readily be apparent to those skilled in the art as reference is made to the detailed description of the preferred embodiment.

5 Detailed Description of the Preferred Embodiment

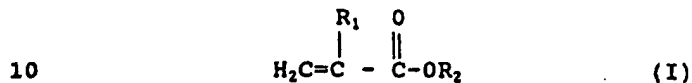
In describing the preferred embodiment, certain terminology will be utilized for the sake of clarity. Such terminology is intended to encompass the recited embodiment, as well as all technical  
10 equivalents which operate in a similar manner for a similar purpose to achieve a similar result.

The ultrafine sized latexes are produced by incrementally adding one or more ethylenically unsaturated monomers capable of  
15 polymerizing in an aqueous environment and incrementally adding a polymerization initiator to a reaction vessel containing water and one or more surfactants and allowing the one or more ethylenically unsaturated monomers to polymerize such that the average particle size of said polymerized monomers is less than 100 nanometers. The  
20 term "incremental addition" defines any form of addition of a small amount of the total monomer and/or initiator to the aqueous solution over an extended period of time until all of the monomer and initiator solutions have been added. This includes cyclic additions, interrupted additions, combinations of the above and the  
25 like. Preferably, the addition of the monomer and initiator is continuous and at a constant level over a period of time.

Any ethylenically unsaturated monomer which is capable of polymerizing in an aqueous environment may be selected as a  
30 starting material. Particularly preferred are any of the following monomers: (meth)acrylic based acids and esters, acrylonitrile, styrene, divinylbenzene, vinyl acetate, ethylenically unsaturated carboxylic acids, acrylamide, methacrylamide, vinylidene chloride, butadiene and vinyl chloride. The dispersion solids that are  
35 produced may take the form of homopolymers (i.e., only one type of

monomer selected) or copolymers (i.e., mixtures of two or more types of monomer are selected; this specifically includes terpolymers and polymers derived from four or more monomers).

- 5 Most preferred are the use of acrylic based acids and esters. The acrylic polymers of the present invention are derived from one or more acrylate monomers having the formula



where R<sub>1</sub> is preferably hydrogen or an alkyl group having from 1 to 4 carbon atoms and R<sub>2</sub> is an aliphatic group having from 1 to 20 carbon atoms. In most preferred embodiments, R<sub>1</sub> comprises a methyl group and R<sub>2</sub> is an alkyl group having from 1 to 20 carbon atoms.

Specifically useful monomers falling within the scope of formula (I) include methyl methacrylate, ethyl acrylate, butyl acrylate, methacrylic acid, acrylic acid and mixtures thereof.

20 Other monomers or starting compounds which may be utilized to produce ultrafine sized latexes are well known to the art. Examples are set forth in The Encyclopedia of Chemical Technology, Kirk-Othmer, John Wiley & Sons, Vol. 14, pp 82-97, (1981). To the extent necessary, this passage is hereby incorporated by reference.

When producing copolymers that are in part derived from acrylic monomers, the amount of acrylic monomer typically ranges from about 30 to about 99 percent of the total amount of monomers, with amounts ranging from about 50 to about 90 percent being more preferred, and amounts ranging from about 60 to about 80 percent being most preferred. In addition, when copolymerizing with an acid, such as methacrylic acid, the copolymer may include up to 60 weight percent of acid. This is much higher than prior art systems and enables the latexes to be particularly useful in textile

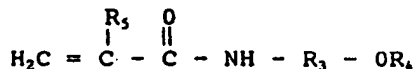


applications as the resulting materials are easier to dissolve in base. Further, when producing copolymer dispersions, the separate monomers may be fed to the aqueous reaction medium from either the same or different feed vessels.

5

For several applications, while not necessary, it may be desirable that the polymers produced be cross-linked. This is accomplished by adding one or more cross-linking agents to the reaction medium. Examples of cross linking agent include monofunctional compounds such as N-alkylol amides of the formula

10



15

where  $\text{R}_3$  is an alkyl group having from 1 to 10 carbon atoms, preferably from 1 to 4 carbon atoms;  $\text{R}_4$  is hydrogen or an alkyl group having from 1 to 10 carbon atoms, preferably from 1 to 4 carbon atoms; and  $\text{R}_5$  is hydrogen or an alkyl group having from 1 to 4 carbon atoms. Specific examples of suitable cross-linking agents include N-methylol acrylamide, N-ethanol acrylamide, N-propanol acrylamide, N-methylol maleimide, N-ethylol maleamide, N-methylol maleamic acid, N-methylol maleamic acid esters, the N-alkylol amides of the vinyl aromatic acids such as N-methylol-p-vinyl benzamide, and the like. Another useful cross-linking agent is N-(isobutoxymethyl) acrylamide.

25

30

Various difunctional compounds or monomers can also be utilized as effective cross-linking agents. These include compounds containing two olefinic groups such as divinylbenzene, divinyl naphthalene, divinylcyclohexane, and the like; various diacrylate or dimethacrylate esters of aliphatic diols where the ester portion has from 1 to 10 carbon atoms, and is preferably alkyl where the diol portion has from 2 to 8 carbon atoms. Examples of these materials include ethylene glycol dimethacrylate, diethylene glycol diacrylate, diethylene glycol dimethacrylate and butylene glycol.

Other cross-linking agents are described in the Journal of Applied Polymer Science, Vol. 34, pp 2389-2397 (1987) John Wiley & Sons, Inc., in an article entitled "New Cross-Linking Agents for Vinyl Polymers". To the extent necessary, this article is hereby fully  
5 incorporated by reference.

The amount of the cross linking agent when utilized is generally from about 0.05 to about 10 percent by weight, desirably from about 0.1 to about 5 percent by weight, and most preferably from about  
10 0.1 to about 1.0 percent by weight based upon the total weight of all monomers added.

Also incrementally added to the aqueous reaction medium is one or more polymerization initiators, preferably a free radical thermal  
15 initiator. The polymerization initiator may take the form of many known initiators such as azo, peroxide, persulfate and perester initiators and may be either water soluble or monomer soluble. The amount of initiator added to the solution typically ranges from between about .05 to about 2 weight percent of the emulsion with  
20 amounts ranging from about 0.1 to about 1.0 weight percent being particularly preferred and amounts ranging from about 0.1 to about 0.5 weight percent being most preferred. The free radical initiator added is preferably an azo (azobisnitrile) type initiator (water or oil soluble) such as 2,2'-azobis-isobutyronitrile, 2,2'-  
25 azobis-(2-methylpropanenitrile), 2,2'-azobis-(2,4-dimethylpentanenitrile), 2,2'-azobis-(2-methylbutanenitrile), 1,1'-azobis-(cyclohexanecarbonitrile), 2,2'-azobis-(2,4-dimethyl-4-methoxyvaleronitrile), 2,2'-azobis-(2,4-dimethylvaleronitrile) and 2,2'-azobis-(2-amidinopropane) hydrochloride.

Other free radical initiators which may be selected include peroxide materials such as benzoyl peroxide, cumene hydroperoxide, hydrogen peroxide, acetyl peroxide, lauroyl peroxide, persulfate materials such as ammonium persulfate, and peresters such as t-  
35 butylperoxypivalate,  $\alpha$ -cumylperoxypivalate and t-butylperoctoate.

Examples of commercially suitable initiators which may be selected include Wako V-50, Vazo 52, Vazo 64, Vazo 67 and Lupersol 11. These commercial initiators may be included with the monomer feed.

5

In the case of water soluble initiators, such as the peroxides and persulfates, it is critical that during polymerization the ionicity of the reaction medium be maintained at a constant. This is accomplished by removing a portion of the water from the aqueous reaction medium and adding this removed water to the initiator feed stream. The need for maintaining a constant ionicity is seen when attempting a conventional post treatment for residual monomer with ammonium persulfate and sodium metabisulfite. Large quantities of coagulum form, reducing the efficacy of the process. Similarly, a conventional initiator feed consisting of ammonium persulfate and 1-3 weight percent of the total water volume will cause agglomeration of polymer particles throughout the initiator addition.

It has been found that by maintaining a constant ionicity in the reaction mixture, agglomeration can be avoided, yielding a more uniform particle size emulsion. By diluting the water soluble initiator with the proper quantity of water, the ionic strength of the initiator system will be the same as the contents of the reaction vessel at any time during the reaction/initiator feed. Presumably, this matched ionicity (as expressed in the number of charges per volume) allows the diffusion controlled migration of charged species such as ammonium persulfate and ionic surfactants from droplet to reaction mixture or vice versa.

30

Use of highly concentrated initiator solutions presumably allows large changes in the ionic concentration in the area immediately surrounding an initiator droplet. It is hypothesized that this massive change in charge density overwhelms the stabilizing forces exerted on the particles by surfactant and initiator residues.

35

The same ionic balance can be achieved by careful selection of a charge neutral monomer soluble initiator such as the azo type initiator commercially sold as VAZO 52 (2,2'-azobis-(2,4-dimethylvaleronitrile)) or VAZO 64 (2,2'-azobis-isobutyronitrile).  
5 In these cases, the entire quantity of initiator is contained within the monomer feed.

It is believed that the concept of maintaining a constant ionicity in the reaction medium has not been utilized to form uniform sized  
10 ultrafine polymer latexes until the present invention. The prior art in the field of ultrafine sized latexes teaches that the initiator be either contained within the aqueous reaction vessel or added as a "single shot".

15 In accordance with the process of the present invention, the monomer(s) and initiator(s) are fed into an aqueous reaction medium which comprises water and at least one or more emulsifiers. The emulsifiers are generally surfactants and hence can be cationic, nonionic, anionic, amphoteric, copolymerizable surfactants and the  
20 like with anionic generally being desired. Generally, the type of emulsifiers utilized are those which can be utilized in conventional latex polymerizations. As is recognized by one skilled in the art, a key criteria for selecting a surfactant is its compatibility with the initiator.

25 Examples of suitable amphoteric surfactants include the alkali metal, alkaline earth metal, ammonium or substituted ammonium salts of alkyl amphocarboxy glycinate and alkyl amphocarboxypropionates, alkyl amphodipropionates, alkyl amphodiacetates, alkyl  
30 amphoglycinates and alkyl amphopropionates wherein alkyl represents an alkyl group having 6 to 20 carbon atoms. Other suitable amphoteric surfactants include alkyliminopropionates, alkyl iminodipropionates and alkyl amphopropylsulfonates having between 12 and 18 carbon atoms, alkylbetaines and amidopropylbetaines and  
35 alkylsultaines and alkylamidopropylhydroxy sultaines wherein alkyl

represents an alkyl group having 6 to 20 carbon atoms.

5 Anionic surfactants which may be selected include any of the known hydrophobes attached to a carboxylate, sulfonate, sulfate or phosphate solubilizing group including salts. Salts may be the sodium, potassium, calcium, magnesium, barium, iron, ammonium and amine salts of such surfactants.

10 Examples of such anionic surfactants include water soluble salts of alkyl benzene sulfonates having between 8 and 22 carbon atoms in the alkyl group, alkyl ether sulfates having between 8 and 22 carbon atoms in the alkyl group, alkali metal, ammonium and alkanolammonium salts or organic sulfuric reaction products having  
15 in their molecular structure an alkyl, or alkaryl group containing from 8 to 22 carbon atoms and a sulfonic or sulfuric acid ester group.

Preferred are linear sodium and potassium alkyl sulfates. Particularly preferred is the use of sodium lauryl sulfate (sodium  
20 dodecyl sulfate). Another preferred type of anionic surfactant are alkyl benzene sulfonates, in which the alkyl group contains between about 9 to about 15, and even more preferably, between about 11 to about 13 carbon atoms in a straight chain or branched chain configuration and even most preferred a linear straight chain  
25 having an average alkyl group of about 11 carbon atoms.

In some embodiments, mixtures of anionic surfactants may be utilized, with mixtures of alkyl or alkylaryl sulfonate and sulfate surfactants being especially preferred. Such embodiments comprise  
30 a mixture of alkali metal salts, preferably sodium salts, of alkyl benzene sulfonates having from about 9 to 15, and more preferred between 11 and 13 carbon atoms with an alkali metal salt, preferably sodium, of an alkyl sulfate or alkyl ethoxy sulfate having 10 to 20 and preferably 12 to 18 carbon atoms and an average  
35 ethoxylation of 2 to 4.

Specific anionic surfactants which may be selected include linear alkyl benzene sulfonates such as dodecylbenzene sulfonate, decylbenzene sulfonate, undecylbenzene sulfonate, tridecylbenzene sulfonate, nonylbenzene sulfonate and the sodium, potassium, ammonium, triethanolammonium and isopropylammonium salts thereof.

10 Examples of useful nonionic surfactants include condensates of ethylene oxide with a hydrophobic moiety which has an average hydrophilic lipophilic balance (HLB) between about 8 to about 16, and more preferably, between about 10 and about 12.5. These surfactants include the condensation products of primary or secondary aliphatic alcohols having from about 8 to about 24 carbon atoms, in either straight or branched chain configuration, with from about 2 to about 40, and preferably between about 2 and about 15 9 moles of ethylene oxide per mole of alcohol.

Other suitable nonionic surfactants include the condensation products of about 6 to about 12 carbon atom alkyl phenols with about 3 to about 30, and preferably between about 5 and about 14 20 moles of ethylene oxide. Examples of such surfactants are sold under the trade names Igepol CO 530, Igepol CO 630, Igepol CO 720 and Igepol CO 730 by Rhone-Poulenc Inc. Still other suitable nonionic surfactants are described in U.S. Patent No. 3,976,586. To the extent necessary, this patent is expressly incorporated by 25 reference.

Examples of cationic surfactants include cetyl trimethyl ammonium bromide.

30 Other surfactants which may be used include those described in McCutcheons, "Detergents and Emulsifiers," 1978, North American Edition, Published by McCutcheon's Division, MC Publishing Corp., Glen Rock, New Jersey, UESTA., as well as the various subsequent editions. To the extent necessary, this reference is expressly 35 incorporated by reference.

In practice the amount of surfactant present in the aqueous phase ranges between about 0.5 to about 6.3 percent by weight of the monomers added. Amounts between about 0.5 and about 3.0 percent by weight of the total monomers added are more preferred and amounts  
5 between about 1.0 and about 3.0 percent by weight of the total monomers added are most preferred. In general, the particle size of the latex decreases with increasing amounts of surfactant added up to about 3.0 weight percent. Beyond 3.0 weight percent surfactant, the decrease in particle size is far less pronounced.

10

The reaction medium can include between about 0.5 to about 10.0 percent by weight of the monomers added of other optional additives to provide specific functional properties to the final latex. Examples of such additives include plasticizers such as  
15 polyethylene glycol, defoamers, pigments, colorants and dyes, antibacterials, perfumes, pharmaceuticals, enzymes and other biologically active agents, agricultural chemicals, ultraviolet active agents, stabilizers and rheology modifiers.

20

To produce the novel latexes of the present invention a semi-continuous or continuous polymerization process is utilized. This involves adding the monomer, including cross-linking agent if necessary and initiator solutions incrementally to the reaction vessel, which is typically heated to temperatures between about  
25 45°C and about 90°C and includes water and one or more emulsifiers over a period of time as opposed to a batchwise addition. Optionally, the reaction vessel can contain a small amount of monomer before commencement of the incremental polymerization to act as a "seed". Such a small amount of monomer is generally below  
30 30 percent by weight and desirably no more than about 10 percent by weight of the total monomer utilized. The rate of the monomer addition is generally governed by various factors such as reaction vessel size, exothermic reaction temperature increase, cooling capacity of the reaction vessel, and the like, such that the  
35 reaction temperature is generally maintained at a specific value or

range.

The amount of the one or more emulsifiers generally contained in the reaction vessel is generally at least 50 or 60 percent by weight, desirably at least 70 percent by weight, more desirably at least 80 percent by weight, and preferably at least 90 percent by weight of the total amount of emulsifiers. The remaining emulsifier, if any, is fed with either the monomer or initiator feed streams.

The reaction vessel may be maintained at temperatures as low as ambient temperatures (10°C to 20°) up to the boiling point of the aqueous solution. The reaction pressure is generally atmospheric, but may be elevated if necessary to assist in polymerization.

As discussed above, the monomer feed and the initiator feed may be the same feed if the initiator is monomer soluble. Further, if the initiator is water soluble and charged, such as ammonium persulfate, it is fed such that the ionicity throughout the reaction vessel is maintained at a constant. This is typically accomplished by initially transferring an amount of the water from the reaction vessel to the initiator feed to create ionic concentrations in both the feed vessel and the reaction vessel which are substantially equal.

Feeding the initiator solution on an incremental basis provides for a generally steady state free radical concentration throughout the monomer addition. This steady state free radical concentration avoids the low radical concentrations seen with single charges of initiators and prolonged feed times. It is this continual and ready availability of free radicals that allows new chain and particle formation to compete effectively with addition of monomer to existing particles. As compared to prior art single shot initiator feed systems, the inventive process markedly improves the monodispersity of the resulting latex.



Polymerization continues until all of the monomer(s) and initiator has been added into the reaction vessel and until nearly all of the monomer feed has been converted to a polymerized form. Polymerization is generally continued until a high conversion is achieved as in excess of 80 percent, desirably at least 90 or 95 percent, and preferably at least 98 percent or even complete conversion.

Regardless of the particular type of monomers selected for polymerization in the process as set forth above, the polymer average particle size is very small. By the term "particle size" it is meant the volume average median particle size as measured by photocorellation spectroscopy. Polymeric latexes produced according to the present invention have a very small volume average particle size of 100 nanometers or less, with average preferred particle sizes of between about 1 and about 60 nanometers, more preferred between about 5 and about 40 nanometers, still more preferred between about 10 and about 30 nanometers, and ideally between about 10 and about 20 nanometers. Generally, any of the above particle size ranges can be produced depending upon the specific end properties desired.

Further, and particularly because of the incremental initiator feed system used, the range of the produced particle size range is limited. In practice the standard deviation for each desired size latex is no more than 4 nanometers.

The above process yields a polymeric latex which is coagulation stable inasmuch as it can be diluted with water without coagulation occurring. The solids content of the latex is relatively high as from about 5 percent to about 55 percent by weight, desirably from about 15 percent to about 50 percent by weight, more preferably from about 20 to about 40 percent by weight, and most preferably from about 25 to about 35 percent by weight based upon the total weight of the aqueous polymeric latex.

The properties of the polymeric latex are largely dependent upon the monomers selected for polymerization. For example the glass transition temperature of the polymers can range from about -54°C to greater than 130°C.

5

The polymeric latexes of the present invention, due to their extremely fine size, are useful in many applications such as wood preservatives, polymer and metal coatings, adhesives, waterproofing chemicals, textile sizes, agricultural chemicals, pharmaceuticals, oil field chemicals, inks, paper making, rheology modifiers, cosmetics, personal care products, ultraviolet light scatterers and sunscreens, biomedical and immunoassay applications. Even though they are latexes in structure, they often approximate solution type properties. In addition, they may be used alone or in combination with other materials, such as higher mean particle size emulsions to yield products having specifically designed uses.

10

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The invention will be better understood by reference to the following examples.

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Example 1

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An aqueous polymeric latex of methyl methacrylate is prepared as follows: 100 parts per hundred (PHM) methyl methacrylate are mixed with 0.5 PHM VAZO 52, a thermal initiator (2,2'-azobis-(2,4-dimethylvaleronitrile)) soluble in methyl methacrylate. This monomer/initiator solution is metered evenly over 3 hours into a 1-liter glass reaction vessel which contains 185 PHM water and 3 PHM sodium dodecyl sulfate. The reactor is maintained at 85°C and constantly stirred. At the end of the monomer addition, the reactor is maintained at 85°C for another 1 hour. The reaction mixture is then brought to almost complete conversion by treatment with 0.015 PHM t-butyl hydroperoxide and 0.015 PHM sodium metabisulfite, at a temperature of 62°C. This synthesis results in an aqueous polymeric latex containing 35 weight percent solids. The average particle size measured by a Niacomp 370A is 14

nanometers. This polymeric latex is translucent due to the small particle size of the latex particles. The latex is blue in color and has a  $T_g$  of about 105°C.

5

Example 2

An aqueous polymeric latex of butyl acrylate, methyl methacrylate and methacrylic acid is prepared using the same method as in Example 1. The composition of the monomer/initiator solution is 65 PHM butyl acrylate, 25 PHM methacrylic acid, 10 PHM methyl methacrylate, and 1 PHM VA20-64 (2,2'-azobis-isobutyronitrile). This process yields a latex of 25 weight percent total solids and a volume weighted mean particle size of 14 nanometers. The latex is clear, blue in color, and has a  $T_g$  of about -5°C.

15

Example 3

An aqueous polymeric latex of styrene, butyl acrylate and methacrylic acid is prepared as follows: 65 PHM butyl acrylate, 25 PHM methacrylic acid and 10 PHM styrene are thoroughly mixed together to form one feed solution. In a separate feed vessel, 0.25 PHM ammonium peroxydisulfate is added to 65 PHM water. In a separate reaction vessel 3 PHM sodium dodecyl sulfate is added to 244 PHM water and heated to 85°C with continuous stirring. The reason for preparing the separate aqueous initiator solution is to enable a constant ionicity in the reaction vessel throughout the synthesis procedure. Ten percent of the total volume of the ammonium peroxydisulfate solution is added to the heated mixture and the initiator and monomer solutions begin feeding at a rate that allows even metering of the feed solutions over a three hour interval. The reaction mixture is stirred for an additional 30 minutes and subsequently cooled to 62°C. 0.10 PHM sodium metabisulfite is dissolved in 24 PHM water and metered into the reaction mixture over a 1 hour interval. The reaction temperature

is then increased to 85°C for 1 hour. The mixture is then cooled to room temperature and filtered. This charge results in an aqueous polymeric latex containing 23.3 weight percent solids. The volume median particle size measured by photocorrelation spectroscopy is 34 nanometers. The latex is clear, blue in color, and has a  $T_g$  of about -5°C.

#### Example 4

To a solution containing 4.17 PHM of sodium lauryl sulfate and 313 PHM water is added 0.25 PHM ammonium persulfate dissolved in 0.52 PHM water. After an initiation period of five minutes a mixture of 53 PHM butyl acrylate and 47 PHM methyl methacrylate is metered into the solution over an interval of 2 hours. The temperature is then raised to 92°C for 1/2 hour then subsequently cooled and filtered. A blue-gray latex is yielded having a solids level of 24.85%. This latex has an average particle size of less than 30 nanometers and has a  $T_g$  of -5°C.

#### Example 5

To a solution containing 2.57 PHM sodium lauryl sulfate and 241 PHM water is added 0.15 PHM ammonium persulfate dissolved in 0.3 PHM water. After an initiation period of five minutes a mixture of 43 PHM butyl acrylate and 57 PHM methyl methacrylate is metered into the solution over an interval of 2 hours. The temperature is then raised to 92°C for 1/2 hour then subsequently cooled and filtered. A blue-gray latex is yielded at a solids level of 23.10%. This latex has an average particle size of less than 30 nanometers and has a  $T_g$  of 0°C.

#### Example 6

To a solution containing 3.1 PHM sodium lauryl sulfate and 245 PHM water heated to 85°C are added continuously and simultaneously two

separate feeds. One feed is comprised of 0.32 PHM ammonium persulfate dissolved in 85 PHM of water and the other feed is comprised of 10 PHM of styrene, 25 PHM methacrylic acid, and 65PHM butyl acrylate. Feeding of each separate feed occurs for approximately 2.5 hours and each feed stream is metered into the reaction vessel in such a way that both feed streams are completed depleted after approximately 2-5 hours. A solution containing 0.1 PHM sodium metabisulfite dissolved in 24 PHM water is then metered into the reaction mixture over an interval of 1/2 hour. The temperature is maintained for 1 hour and the reaction mixture is subsequently cooled to room temperature and is filtered. A blue-clear latex is yielded having a solids level of 23.3% and an average particle size of about 14 nanometers.

15                   **QUANTITATIVE AND QUALITATIVE TESTING**

Wood Penetration Properties

20           A test is performed to determine the wood penetration ability of the inventive latexes versus commercially available products. The following test procedure is used:

- 25           1. 10% solids solutions of each latex are prepared by diluting each latex with an appropriate amount of distilled water.
2. A pine dowel is cut into 3 inch sections and each dowel is immersed in each latex solution for 3 hours.
- 30           3. Each dowel is dried at ambient conditions overnight.
4. A 2% Nigrosine stain solution is prepared and each dried dowel is immersed in the solution for 24 hours.
- 35           5. Each dowel is removed and dried at ambient conditions

overnight.

6. Cross-sectional pieces of each dowel are cut and evaluated for stain penetration.

5

The sample latexes tested are:

Sample A: Example 4 Latex

Sample B: Example 5 Latex

10 Sample C: Joncryl 537, 46% solids neat (S. C. Johnson)

Sample D: Reichhold 40-423, 46% solids neat (Reichhold Chemical)

Sample E: UCAR 429, 47% solids neat (Union Carbide)

15 The particle size and relative penetration of the stain for each sample is shown in Table 1:

Table 1

	<u>Sample</u>	<u>Particle Size</u>	<u>Penetration</u>
5	A	<30 nm	minimal
	B	<30 nm	minimal
	C	90 nm	slight
	D	100 nm	appreciable
	E	150 nm	extensive

10

The minimal penetration seen when utilizing the inventive materials demonstrates that the smaller particle sized latexes penetrate wood better than conventional latexes. Accordingly, the inventive materials form significantly better wood protective coatings than commercial materials.

15

Surface Tension Properties

The surface tensions of 10 percent solids solutions of Samples A, C, D and E are analyzed using a SensaDyne bubble surface tensiometer. The results are shown in Table 2. The measure for surface tension is in dynes/cm.

20

Table 2

25

	<u>Sample</u>	<u>Particle Size</u>	<u>Surface Tension</u>
	A	<30 nm	57.3
	C	90 nm	40.8
	D	100 nm	57.2
30	E	150 nm	47.9

30

35

Penetrating ability is highly dependent upon wetting ability. If a product does not wet a surface well, it will have little chance of penetrating the surface. The higher surface tension of Sample A, the inventive sample, places this product at a distinct

disadvantage in penetration studies. However, the previous Example demonstrates that Sample A has much better wood penetration than the commercial samples (C, D and E). Thus, it is hypothesized that the particle size of the samples is much more important than surface tension in determining the penetrating ability of a latex. In addition, the above tests are performed using 10% solids solutions. It is theorized that when using the Samples in a "neat" form that Samples A and B would demonstrate even more enhanced positive results.

#### Textile Sizing Properties

The latex of Example 6 is compared with the commercial products Permaloid 150 and Permaloid 172, both manufactured by Rhône-Poulenc Inc. for use as textile sizes. All samples are evaluated at concentrations of 7% and applied to polyester filament yarn via a lab scale slasher. The abrasion resistance of the latex of Example 6 is approximately equal to that of Permaloid 150 and Permaloid 172. The advantage rendered by use of the inventive latex is the absence of neutralization prior to application. Conventional sizes, such as Permaloid 150 and Permaloid 172, are applied as solution polymers prepared by the alkali induced solubilization of a conventional latex polymer. The inventive ultrafine latex based textile sizes are applied directly to the yarn without neutralization. This eliminates the need for alkali or the monitoring of ammonia release normally associated with the sizing of filament yarns and hence provides significant advantages as compared to commercially available materials.

Having described the invention in detail and by reference to the preferred embodiments thereof, it will be apparent that modifications and variations are possible without departing from the scope of the appended claims.